

Pressure and surface tension of an active simple liquid: a comparison between kinetic, mechanical and free-energy based approaches.

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We discuss different definitions of pressure for a system of active spherical particles driven by a non-thermal coloured noise. We show that mechanical, kinetic and free-energy based approaches lead to the same result up to first order in the non-equilibrium expansion parameter. The first prescription is based on a generalisation of the kinetic mesoscopic virial equation and expresses the pressure exerted on the walls in terms of the average of the virial of the inter-particle forces. In the second approach, the pressure and the surface tension are identified with the volume and area derivatives, respectively, of the partition function associated with the known stationary non-equilibrium distribution of the model. The third method is a mechanical approach and is related to the work necessary to deform the system. The pressure is obtained by comparing the expression of the work in terms of local stress and strain with the corresponding expression in terms of microscopic distribution. This is determined from the force balance encoded in the Born-Green-Yvon equation. Such a method has the advantage of giving a formula for the local pressure tensor and the surface tension even in inhomogeneous situations. By direct inspection, we show that the three procedures lead to the same values of the pressure, and give support to the idea that the partition function, obtained via the unified coloured noise approximation, is more than a formal property of the system, but determines the stationary non-equilibrium thermodynamics of the model.

I. INTRODUCTION

Temperature, density and pressure are important and measurable quantities characterising the macro-state of a system at equilibrium. In particular, the pressure is both a mechanical and a thermodynamic property since it measures the force necessary to confine a system and plays a major role in the equation of state. It can be obtained in different ways: a) mechanically, by measuring the average normal force per unit of surface, that is the rate of momentum transferred to a surface per unit area, b) by kinetic theory using the Clausius virial theorem or c) by measuring the isothermal variation of the Helmholtz free energy with respect to the volume available to the system. The three methods give the same results as far as equilibrium systems are concerned, whereas in the case of non-equilibrium systems the situation is not so simple and such an equivalence cannot be proved in general since the third method requires the existence and the knowledge of an off-equilibrium thermodynamic potential. The issue is of particular importance, nowadays, when we consider the behavior of active fluids which are forced out of equilibrium by injecting energy at the individual particle level, in contrast to a driven system where the forcing occurs at the boundaries of the system¹⁻³. In active fluids, is even delicate to define a pressure that is not a mechanical pressure and for instance it has been demonstrated that the pressure measured at a wall is not necessarily the same as the pressure measured in the bulk of a system⁴. However, we can show that for a particular active fluid model it is possible to prove that the three methods give equivalent answers. The virial method⁵ is particularly useful when one wishes to derive the pressure from a numerical simulation^{6,7} or from a mesoscopic description such as the Fokker-Planck equation⁸.

In thermodynamics, the pressure can be obtained as the negative of the derivative of the Helmholtz free energy, \mathcal{F} , with respect to the volume at constant temperature and number of particles. In equilibrium statistical mechanics this translates into the analogous volume derivative of the logarithm of the canonical partition function. In stationary out-of-equilibrium active systems, the existence of \mathcal{F} cannot be proved in general. However, the Gaussian colored noise model in the unified colored noise approximation (UCNA)⁹ is a notable exception. For this model, the N-particle distribution function is known and has a form similar to the Gibbs distribution of an equilibrium system. Thus, in principle, we can formally define a partition function as the classical trace of such a distribution and obtain from it a series of derived quantities, such as a "thermodynamic" pressure. It is then natural to ask: does this object has the required properties and, more importantly, does it coincide with the mechanical and the virial pressure?

A third route to determine the pressure considers the hydrodynamic equations and under conditions of zero fluxes and the fact that the divergence of the pressure tensor must satisfy a mechanical balance or hydrostatic equilibrium condition: it means that the internal stress of the fluid must balance the resultant of the body forces. Such a mechanical equilibrium condition allows determining the pressure tensor in terms of the microscopic distribution functions.

We prove that the three methods lead to the same expression of the pressure if we limit ourselves to the first order in the non-equilibrium parameter τ , i.e. the persistence time of the "self-propulsion". At higher order, however, we show how this proof cannot be readily extended since the hydrostatic equation involves a matrix inversion which can be performed only up to the first order in the perturbing parameter. On the other hand, the present result seems to suggest that studying active particles models, close to equilibrium, allows unifying the thermodynamic with the mechanical approach to pressure.

The goal of the present paper is to derive explicit expressions for the pressure and the surface tension for self-propelled^{4,10–13} particles using the Gaussian colored noise model in the UCNA approximation which has been recently studied by our group^{14–16}. The paper is organised as follows: in section II we report the main results obtained in previous papers and necessary for the comprehension of the following developments. In section III, we apply the mesoscopic virial equation (MVE) of Falasco et al.⁸ to derive an expression for the pressure exerted on the walls. The method employs the Fokker-Planck equation for the distribution function and the asymptotic constancy of some functions of the coordinates to determine the virial of the force acting on the active fluid. Such an expression for the pressure is compared in section IV with the derivative of the logarithm of the partition function associated with the stationary configurational distribution function. To compute the volume derivative we use a volume scaling method of the free energy employed in equilibrium statistical mechanics to compute the pressure of an assembly of particles. The two results are seen to coincide up to first order in the non-equilibrium parameter, a fact which is not at all trivial, being the first one a mechanical property and the second a statistical property connected to the existence of a thermodynamic potential of the system. As a secondary benefit of the stretching method, we obtain a first definition of the surface tension of the active system. In section V, we proceed further and use the third approach, originally due to Baus and Lovett, to compute the pressure: it uses the concept of mechanical work associated with a local deformation of the system to obtain the pressure and the surface tension. By this approach, it is in principle possible to determine the components of the pressure tensor at every point of the non-uniform fluid by measuring the work necessary to produce a local deformation. Even in this case, it turns out that the value of the predicted pressure is the same as those derived by the two previous approaches and regarding the surface tension we obtain an agreement with the result of section IV. Corroborated by this agreement between the different methods we apply the mechanical method to the calculation of the pressure tensor in an anisotropic case. Finally, in section VI we come to the conclusions and perspectives. In order to render the reading of the present paper easier, we created several appendices where the derivations of some mathematical results used in the main text have been reported.

II. MODEL EQUATIONS

In the Gaussian colored noise model we consider the spatial configurations $(\mathbf{r}_1, \dots, \mathbf{r}_N)$ of a system of overdamped particles subjected to a velocity dependent frictional force $-\gamma\mathbf{v}$, and to a white Gaussian noise of intensity $\sqrt{D_t}$ and Gaussian coloured noise, characterized by intensity $\sqrt{D_a}/\tau$ and relaxation time τ , and enclosed in a bounded region of volume V under stationary conditions and in the absence of currents are approximately described by the following probability measure

$$P_N(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{Z_N} \exp\left(-\frac{\mathcal{H}(\mathbf{r}_1, \dots, \mathbf{r}_N)}{T_s}\right). \quad (1)$$

The distribution (1) is valid under the so-called UCNA approximation and results from replacing the underlying coloured noise non Markovian dynamics with Markovian dynamics with new and more complicated interactions as discussed in previous works^{14,15}. The distribution depends on T_s , an effective temperature, resulting from the sum of a translational temperature $T_t = D_t\gamma$ and a swim temperature $T_a = D_a\gamma$, where D_t and D_a are two coefficients related to the translational and rotational diffusion, respectively^{17–19}. \mathcal{H} is an effective Hamiltonian which is determined in terms of the actual potential energy \mathcal{U}_{total} of the system, detailed in the following, and Z_N is the normalisation and can be viewed as a generalisation to the non-equilibrium stationary regime of the partition function. As shown hereafter, both \mathcal{H} and Z_N reduce to their equilibrium counterparts when the non-equilibrium parameter $\tau/\gamma \rightarrow 0$, or in non-dimensional form when $\frac{\tau}{\gamma\sigma^2}\epsilon \rightarrow 0$, where ϵ and σ are typical energy and length scales characterizing the inter-particle interactions.

In analogy with equilibrium statistical mechanics, we introduce a "thermodynamic" pressure, p_t , as:

$$p_t = T_s \frac{\partial \ln Z_N}{\partial V} \quad (2)$$

and discuss its properties and relationship with other definitions of pressure such as the virial approach where the pressure is defined as the external action necessary to confine the system to a bounded region or the kinetic theory

approach where the pressure is identified with the rate of momentum per unit surface transferred from the colliding particles to the walls.

The potential energy may comprise one body and pairwise potentials and has the form

$$\mathcal{U}_{total}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_i u(\mathbf{r}_i) + \sum_{i>j} w(\mathbf{r}_i - \mathbf{r}_j). \quad (3)$$

The effective potential energy, \mathcal{H} , instead, results from the adiabatic elimination of the fast degrees of freedom and is related to \mathcal{U}_{total} by:

$$\mathcal{H}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \mathcal{U}_{total}(\mathbf{r}_1, \dots, \mathbf{r}_N) + \frac{\tau}{2\gamma} \sum_k^N \left(\frac{\partial \mathcal{U}_{total}(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\partial \mathbf{r}_k} \right)^2 - T_s \ln |\det(\Gamma_{\alpha i, \beta k}(\mathbf{r}_1, \dots, \mathbf{r}_N))| \quad (4)$$

where Greek indexes stand for Cartesian components and the non-dimensional friction matrix Γ is defined as

$$\Gamma_{\alpha i, \beta k}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \delta_{\alpha\beta} \delta_{ik} + \frac{\tau}{\gamma} \frac{\partial^2 \mathcal{U}_{total}(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\partial r_{\alpha i} \partial r_{\beta k}}. \quad (5)$$

The explicit structure of the matrix $\Gamma_{\alpha 1, \beta k}$ follows from (3):

$$\Gamma_{\alpha i, \beta k} = \left(\delta_{\alpha\beta} + \frac{\tau}{\gamma} u_{\alpha\beta}(\mathbf{r}_i) + \frac{\tau}{\gamma} \sum_j w_{\alpha\beta}(\mathbf{r}_i - \mathbf{r}_j) \right) \delta_{ik} - \frac{\tau}{\gamma} w_{\alpha\beta}(\mathbf{r}_i - \mathbf{r}_k) (1 - \delta_{ik}). \quad (6)$$

We remark that the diagonal elements contain $(N - 1)$ pairwise terms whereas the off-diagonal matrix elements just one term. The idea is to show that in the limit of a large number of particles it is possible to neglect the effect presence of the off-diagonal elements.

As shown elsewhere (see ref.¹⁵) assuming that the off-diagonal elements of the Γ matrix are negligible the density distribution $\rho(\mathbf{r})$ satisfies an integrodifferential equation similar to the Born-Green-Yvon (BGY) equation of passive fluids. By the method illustrated in appendix A we find

$$\begin{aligned} T_s \sum_{\beta} \frac{\partial}{\partial r_{\beta}} \left(\left[\delta_{\alpha\beta} - \frac{\tau}{\gamma} u_{\alpha\beta}(\mathbf{r}) \right] \rho(\mathbf{r}) - \frac{\tau}{\gamma} \rho(\mathbf{r}) \int d\mathbf{r}_2 w_{\alpha\beta}(\mathbf{r} - \mathbf{r}_2) \rho(\mathbf{r}_2) g(\mathbf{r}, \mathbf{r}_2) \right) \\ = -\rho(\mathbf{r}) \frac{\partial u(\mathbf{r})}{\partial r_{\alpha}} - \rho(\mathbf{r}) \int d\mathbf{r}_2 \rho(\mathbf{r}_2) g(\mathbf{r}, \mathbf{r}_2) \frac{\partial w(\mathbf{r} - \mathbf{r}_2)}{\partial r_{\alpha}} \end{aligned} \quad (7)$$

where we introduced the pair correlation function $g(\mathbf{r}, \mathbf{r}')$. We shall rewrite (7) in the more compact form:

$$f_{\alpha}(\mathbf{r}) = T_s \sum_{\beta} \frac{\partial}{\partial r_{\beta}} \left[\tilde{\Gamma}_{\alpha\beta}^{-1}(\mathbf{r}) \rho(\mathbf{r}) \right] + \rho(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') g(\mathbf{r}, \mathbf{r}') \frac{\partial w(\mathbf{r} - \mathbf{r}')}{\partial r_{\alpha}}, \quad (8)$$

where $\tilde{\Gamma}^{-1}(\mathbf{r})$ is a $d \times d$ matrix defined by:

$$\tilde{\Gamma}_{\alpha\beta}^{-1}(\mathbf{r}) = \left[\delta_{\alpha\beta} - \frac{\tau}{\gamma} u_{\alpha\beta}(\mathbf{r}) - \frac{\tau}{\gamma} \int d\mathbf{r}' \rho(\mathbf{r}') g(\mathbf{r}, \mathbf{r}') w_{\alpha\beta}(\mathbf{r} - \mathbf{r}') \right]. \quad (9)$$

and $f_{\alpha}(\mathbf{r}) = -\rho(\mathbf{r}) \frac{\partial u(\mathbf{r})}{\partial r_{\alpha}}$ is the external force per unit volume. Let us remark that eq. (8) has the form of a BGY equation and arises from the conservation of linear momentum, that is is equivalent to $\langle \frac{\partial \mathbf{J}}{\partial t} \rangle$, where \mathbf{J} is the momentum density.

In the present theory the matrices Γ and $\tilde{\Gamma}$ play a central role because they describe how the mobility of the particles depends on their environment^{20,21} and both reduce to the identity matrix when the non-equilibrium parameter $\tau/\gamma \rightarrow 0$.

III. KINETIC APPROACH: MESOSCOPIC VIRIAL EQUATION

In this section, we shall use a method inspired by the recent paper by Falasco et al⁸, who derived a virial equation for non-equilibrium systems described by a Fokker-Planck equation. Clausius's virial theorem follows from the fact

that the average of the derivative of a bounded function is zero. In the specific case of the UCNA, the result follows when we consider the derivative of an operator, \mathcal{O} such that it satisfies the following set of differential equations:

$$\frac{\partial \mathcal{O}(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\partial r_{\alpha i}} = \sum_{\delta l} \Gamma_{\alpha i, \delta l} r_{\delta l} \quad (10)$$

A representation of \mathcal{O} , a part an arbitrary and inessential constant, is:

$$\mathcal{O} = \sum_{\alpha i} \left(\frac{r_{\alpha i}^2}{2} + \frac{\tau}{\gamma} \frac{\partial \mathcal{U}_{total}}{\partial r_{\alpha i}} r_{\alpha i} \right) - \frac{\tau}{\gamma} \mathcal{U}_{total} \quad (11)$$

Using (11) and (C2) explicitly we obtain:

$$\frac{d\langle \mathcal{O} \rangle}{dt} = \int d^N \mathbf{r} P_N(\mathbf{r}_1, \dots, \mathbf{r}_N) \sum_{\beta k} \left(\frac{1}{\gamma} F_{\beta k} r_{\beta k} + D \Gamma_{\beta k, \beta k}^{-1} \right) \quad (12)$$

the sums are over all the particles, with locations denoted by \mathbf{r}_i , on which act the forces F_i . Since the particles are bounded by the finite volume V the time average of the l.h.s. will approach zero and we can write by splitting the forces into the external, or confining wall forces, and the inter-particle force:

$$\sum_i^N \langle (\mathbf{F}_i^{ext} + \mathbf{F}_i^{int}) \cdot \mathbf{r}_i \rangle + D \gamma \sum_{\alpha i} \langle \Gamma_{\alpha i, \alpha i}^{-1} \rangle = 0 \quad (13)$$

In the last term the forces are separated in two parts: wall and interparticle forces. The forces exerted by the bounding walls of the container are macroscopically described as external pressure: each element $d\mathbf{A}$ of their area exerts a force $-p_v d\mathbf{A}$ (the subscript V stands for virial) so that

$$\sum_i^N \langle \mathbf{F}_i^{ext} \cdot \mathbf{r}_i \rangle = -p_v \oint \mathbf{r} \cdot d\mathbf{A} = -p_v V d,$$

where \mathbf{r} is the position vector of the surface element and the last equality follows from the application of the divergence theorem. The internal virial is:

$$\sum_i^N \langle \mathbf{F}_i^{int} \cdot \mathbf{r}_i \rangle = \frac{1}{2} \sum_i \sum_j' \langle \mathbf{F}_{ij} \cdot (\mathbf{r}_i - \mathbf{r}_j) \rangle \quad (14)$$

where we have symmetrized the sum. Finally, by approximating the inverse matrix Γ^{-1} using the methods of appendix B we evaluate the trace of the $dN \times dN$ matrix by the following formula:

$$T_s \sum_i^N \sum_{\alpha}^d \langle \Gamma_{\alpha i, \alpha i}^{-1} \rangle \approx T_s \sum_{\alpha}^d \int d\mathbf{r} \tilde{\Gamma}_{\alpha\alpha}^{-1}(\mathbf{r}) \rho(\mathbf{r}) \quad (15)$$

where in the second equality we have used (B1). We, now, write

$$p_v = \frac{T_s}{dV} \sum_{\alpha}^d \int d\mathbf{r} \tilde{\Gamma}_{\alpha\alpha}^{-1}(\mathbf{r}) \rho(\mathbf{r}) - \frac{1}{2dV} \sum_{\alpha}^d \int d\mathbf{r} \int d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}') \frac{\partial w(\mathbf{r} - \mathbf{r}')}{\partial r_{\alpha}} (r_{\alpha} - r'_{\alpha}) \quad (16)$$

where the second term in (16) is analogous to the direct contribution to the pressure in passive fluids stemming from interactions. Using the approximation (9) we obtain the explicit representation

$$\frac{1}{dV} T_s \sum_{\alpha}^d \int d\mathbf{r} \tilde{\Gamma}_{\alpha\alpha}^{-1}(\mathbf{r}) \rho(\mathbf{r}) \approx \frac{T_s}{V} \left[N - \frac{1}{d} \frac{\tau}{\gamma} \int d\mathbf{r} \sum_{\alpha} u_{\alpha\alpha}(\mathbf{r}) \rho(\mathbf{r}) - \frac{1}{d} \frac{\tau}{\gamma} \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') g(\mathbf{r}, \mathbf{r}') \sum_{\alpha} w_{\alpha\alpha}(\mathbf{r} - \mathbf{r}') \right] \quad (17)$$

where the double subscripts indicate second partial derivatives of the potentials with respect to the coordinate r_{α} . The first term in the r.h.s. of (16) contains the ideal gas pressure, $T_t N/V$, stemming from the translational degrees of freedom, the swim pressure, $T_a N/V$, (recall that $T_s = T_t + T_a$) due to the rotational degrees of freedom and the so-called indirect interaction contribution represented by the second and third term in formula (17), which takes into account the slowing down of active fluids near a boundary or in regions of high density. The indirect interaction pressure involves the interplay between the rotational degrees of freedom and the interparticle forces and is a non-equilibrium effect. In fact, in the limit of $\tau \rightarrow 0$ the quantity (17), reduces to $T_t N/V$, the ideal gas contribution to the pressure. Expressions for the pressure equivalent to (16) will be derived by two different approaches in the next sections.

IV. STATISTICAL MECHANICAL APPROACH

The mechanical interpretation of the pressure is not the only one: the pressure and the surface tension are also thermodynamic and statistical observables characterising the macrostate of the system. In this section and in the related appendices D and E we derive their expressions by differentiation of the partition function, Z_N , with respect to the volume and area and verify that these derivatives are equal (within the order allowed by the approximations involved) to the MVE expression. In other words the thermodynamic-like relationship $p_t = -\frac{\partial \mathcal{F}}{\partial V}_{T,N}$, where \mathcal{F} is defined as $\mathcal{F} = -T_s \ln Z_N$ agrees with p_v . As far as the surface tension is concerned the agreement with a method based on the distribution functions is shown in section V.

A. Statistical pressure

The logarithmic derivative with respect to the volume is performed employing a volume scaling procedure as illustrated in appendix D with the following result:

$$p_t = \frac{T_s}{3V} \sum_{\alpha} \sum_i^N \langle \Gamma_{\alpha i, \alpha i}^{-1} \rangle + \frac{1}{6V} \sum_i \sum_j' \langle \mathbf{F}_{ij} \cdot (\mathbf{r}_i - \mathbf{r}_j) \rangle \quad (18)$$

which is the same expression as eq. (16) obtained by using the kinetic method. Moreover, we shall demonstrate that such a definition of pressure coincides (up to order τ/γ) with the pressure obtained by the microscopic condition of hydrostatic equilibrium. Again we can see that the pressure is made up of three contributions: ideal gas and indirect pressure both contained in the first term, as can be seen using eq.(B1), and a direct interparticle interaction pressure term contained in the last term.

B. Statistical surface tension

Buff obtained a formula for the surface tension of equilibrium systems by generalizing the stretching method of the previous section²². We prove that the surface tension obtained through the mechanical definition also satisfies a macroscopic thermodynamic-like relationship $\gamma = -T_s \frac{\partial \ln Z_N}{\partial A}_{T,N}$. Performing the derivative of the configurational integral Z_N requires taking into account that the limits of the integrals defining Z_N depend on the system area, A . A simple calculation reported in appendix E gives:

$$\gamma = \frac{1}{A} \int_V d\mathbf{r}_1 \dots d\mathbf{r}_N P_N(\mathbf{r}_1, \dots, \mathbf{r}_N) \sum_i \left\{ \left[x_i \frac{\partial U_{int}}{\partial x_i} - z_i \frac{\partial U_{int}}{\partial z_i} \right] + T_s \frac{\tau}{\gamma} \left[\frac{\partial^2 \mathcal{U}_{int}}{\partial x_i^2} - \frac{\partial^2 \mathcal{U}_{int}}{\partial z_i^2} \right] \right\} \quad (19)$$

Since \mathcal{U}_{int} is a sum of pair potentials using standard manipulations and eq. (9) we can rewrite the first contribution in the integrand, that we identify with the passive surface tension and obtain:

$$\gamma = \frac{1}{2A} \iint_V d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') g(\mathbf{r}, \mathbf{r}') \left[\frac{Y^2}{R} - \frac{Z^2}{R} \right] \frac{\partial}{\partial R} w(R) + T_s \frac{1}{A} \int_V d\mathbf{r} \rho(\mathbf{r}) \left[\tilde{\Gamma}_{zz}^{-1}(\mathbf{r}) - \tilde{\Gamma}_{xx}^{-1}(\mathbf{r}) \right] \quad (20)$$

with $\mathbf{R} = (X, Y, Z) = (x - x', y - y', z - z')$. In the last term, we have used the expansion of the matrix Γ up to order τ/γ to rewrite the formula for the surface tension. We shall prove below in section V B that the surface tension computed by the stretching method gives the same value as the one computed by using the concept of work necessary to stretch the interface.

To zeroth order in the parameter τ the Kirkwood-Buff formula²³ for the surface tension of a planar interface is recovered, whereas the second term represents the correction due to the activity and is similar to the surface tension found by Bialké et al.²⁴. Notice that in a passive fluid the last term vanishes, because the $\tilde{\Gamma}$ matrix becomes the identity matrix.

V. DISTRIBUTION FUNCTIONS APPROACH

We now develop a method that allows computing the pressure tensor and the surface tension in situations where the fluid can also be inhomogeneous. The starting point is different from the one of the previous section which uses

the Fokker-Planck equation to estimate the virial as in eq. (13). We shall use instead the fact that when the system is perturbed starting from an initial steady non-uniform steady state the work done on the system to produce such a result can be written in two different ways: either in terms of the work done by external forces when the particles are displaced by an infinitesimal amount with respect to their initial positions or expressing the work necessary to produce the same deformation (with respect to the given reference state) in terms of the product of the stress and strain tensors. Whereas in a uniform simple fluid one needs a single scalar quantity such as the relative volume variation to measure its deformation, in a non-uniform fluid the deformation with respect to a reference state is measured by a displacement vector $\delta \mathbf{s}(\mathbf{r})$ ^{25,26}. This method is a generalization to active particles of an approach introduced in the literature of passive fluids by Baus and Lovett. Such a method allows defining the pressure tensor in terms of microscopic molecular distributions with the help of the information contained in the first BGY equation (7).

Once we endow the first BGY equation with a suitable closure, in practice expressing the higher correlations in terms of the density profile and of the pair correlation function, it is in principle possible to determine numerically the density profile. On the other hand, even without a numerical solution of the BGY equation we can make predictions about the relevant observables of the problem, such as the pressure and the surface tension. In equilibrium systems, such quantities are measured unambiguously. Hereafter, we present a mechanical derivation of these two quantities following the method of Baus and Lovett^{27,28}, and derive the pressure by computing the work necessary to produce an infinitesimal compression of the system and the surface tension by computing the work necessary to make an infinitesimal stretching of its surface. In the limit $\tau \rightarrow 0$ both observables become identical to their equilibrium counterparts.

Following the book Elasticity Theory by Landau-Lifshitz²⁹) the relative variation of volume $\delta V/V$ can be expressed in terms of the strain $\delta \epsilon_{\alpha\beta} = \frac{1}{2}(\frac{\partial \delta s_\alpha}{\partial r_\beta} + \frac{\partial \delta s_\beta}{\partial r_\alpha})$ associated with a local displacement $\delta \mathbf{s}(\mathbf{r})$ of the fluid, such that matter at \mathbf{r} is displaced to a new position $\mathbf{r}' = \mathbf{r} + \delta \mathbf{s}(\mathbf{r})$, and the relative volume change³⁰ is: $\frac{\delta V}{V} = \nabla \cdot \delta \mathbf{s}(\mathbf{r})$. The condition of mechanical (hydrostatic) equilibrium in the system dictates that the pressure tensor $p_{\alpha\beta}$ in the absence of currents is subjected to the constraint:

$$\sum_{\beta} \frac{\partial}{\partial r_\beta} p_{\alpha\beta}(\mathbf{r}) = f_\alpha(\mathbf{r}). \quad (21)$$

where $\mathbf{f}(\mathbf{r}) = \rho(\mathbf{r})\mathbf{F}(\mathbf{r})$ is the external force per unit volume responsible for confining the system in space and is a body force. We can express the work done on the system when each particle i is displaced by an amount $\delta \mathbf{s}(\mathbf{r}_i)$ as:

$$\delta W = \int_V d\mathbf{r} \sum_{\alpha} f_\alpha(\mathbf{r}) \delta s_\alpha(\mathbf{r}) + \oint_A dA \sum_{\alpha} t_\alpha(\mathbf{r}) \delta s_\alpha(\mathbf{r}) \quad (22)$$

where $t_\alpha(\mathbf{r}) \equiv -p_{\alpha\beta}(\mathbf{r})n_\beta(\mathbf{r})$ is the α component of the stress vector acting on surface of area A of the system at position, and $\mathbf{n}(\mathbf{r})$ the normal to the surface A at \mathbf{r} . The second term in the r.h.s represents the work done by the surface stress and notice that the minus sign is a consequence of our convention of not introducing the stress, but to use directly the pressure tensor which is minus the stress tensor. Following Landau-Lifshitz let us imagine, now, that the system is undeformed at infinity and remove at infinity the surface where the integral is performed so that the second term in the r.h.s of (22) vanishes and only the first term remains. On the other hand, the work (22) can also be expressed in terms of the pressure tensor by using (21) :

$$\delta W = \int_V d\mathbf{r} \sum_{\alpha\beta} \frac{\partial}{\partial r_\beta} p_{\alpha\beta}(\mathbf{r}) \delta s_\alpha(\mathbf{r}) \quad (23)$$

As a consequence of $\oint_A dA \sum_{\alpha} t_\alpha(\mathbf{r}) \delta s_\alpha(\mathbf{r}) = 0$, we finally rewrite the work in terms of the strain and of the pressure tensor, $p_{\alpha\beta}$.

$$\delta W = - \int_V d\mathbf{r} \sum_{\alpha\beta} p_{\alpha\beta}(\mathbf{r}) \delta \epsilon_{\alpha\beta}(\mathbf{r}) \quad (24)$$

In order to obtain an expression for the bulk pressure in a uniform and isotropic system, where $p_{\alpha\beta}(\mathbf{r}) = p_V \delta_{\alpha\beta}$, we, now, assume the deformation to be a uniform infinitesimal dilatation $\delta \mathbf{s}(\mathbf{r}) = \lambda \mathbf{r}$, corresponding to a relative volume change $\frac{\delta V}{V} = 3\lambda$. According to (24) the work of deformation is $\delta W = -\lambda \int_V d\mathbf{r} \sum_{\alpha} p_{\alpha\alpha}(\mathbf{r}) = -3\lambda p_V V$. On the other hand, by computing the work using the body force we obtain: $\delta W = \lambda \int_V d^3\mathbf{r} \rho(\mathbf{r})\mathbf{F}(\mathbf{r}) \cdot \mathbf{r}$, and by equating these last two expressions we find the volume averaged pressure

$$p_V = -\frac{1}{3V} \int_V d\mathbf{r} \rho(\mathbf{r})\mathbf{F}(\mathbf{r}) \cdot \mathbf{r}. \quad (25)$$

Finally, with the help of the BGY equation (8) we eliminate $\rho(\mathbf{r})\mathbf{F}(\mathbf{r})$, substitute in (25): and express the pressure in terms of molecular distributions:

$$p_V = -\frac{T_s}{3V} \int d\mathbf{r} \sum_{\alpha\beta} \frac{\partial}{\partial r_\beta} [\tilde{\Gamma}_{\alpha\beta}^{-1}(\mathbf{r})\rho(\mathbf{r})] r_\alpha - \frac{1}{3V} \int d\mathbf{r} \int d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}') \sum_{\alpha} \frac{\partial w(\mathbf{r} - \mathbf{r}')}{\partial r_\alpha} r_\alpha \quad (26)$$

Similarly to eq. (16), the first term in equation (26), that in the following we shall call "active" for short, is the sum of three contributions: ideal gas, swim and indirect contribution. It can be integrated by parts and, after discarding a surface term becomes

$$p_V^{active} = \frac{T_s}{3V} \sum_{\alpha} \int d\mathbf{r} \tilde{\Gamma}_{\alpha\alpha}^{-1}(\mathbf{r})\rho(\mathbf{r}) \quad (27)$$

and turns out to have the same form as (17). The second term in the left hand side of eq. (26), instead, represents the so-called direct interaction term due to intermolecular forces and can be expressed as:

$$p_V^{direct} = -\frac{1}{6V} \int d\mathbf{r} \int d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}') \sum_{\alpha} (r_\alpha - r'_\alpha) \frac{\partial w(\mathbf{r} - \mathbf{r}')}{\partial r_\alpha} \quad (28)$$

while the total pressure is given by the sum $p_V = p_V^{active} + p_V^{direct}$ and is the same as the MVE result of (16) and thus to (18).

The work of deformation method, which yields the same result for the pressure of a uniform system as the MVE approach of section III, will be now applied hereafter to two different non-uniform situations: a) an active fluid in the presence of a flat boundary and b) in the presence of an interface between two phases.

A. Pressure against a planar wall

We represent a wall by means of an external soft-repulsive potential $u(\mathbf{r})$ rapidly decaying away from the wall and derive the corresponding expression of the pressure tensor. In this case, we consider an anisotropic deformation, $\delta\mathbf{s}(\mathbf{r})$, affecting only the direction normal to the wall, and to this purpose choose a different parametrization. To include the planar wall we consider a cubic system

$$0 \leq z \leq L_z; \quad -\frac{1}{2}L_x \leq x \leq \frac{1}{2}L_x; \quad -\frac{1}{2}L_y \leq y \leq \frac{1}{2}L_y \quad (29)$$

and locate the wall at $z = 0$. The displacement field is now represent by $\delta\mathbf{s}(\mathbf{r}) = (0, 0, \lambda(z - \bar{z})\theta(z - \bar{z}))$ and the associated volume change reads: $\delta V = \int d\mathbf{r} \nabla \cdot \delta\mathbf{s}(\mathbf{r}) = \lambda L_x L_y (L_z - \bar{z})$, where $z = \bar{z}$ denotes a reference plane inside the system, where $\mathbf{f}(\mathbf{r})$ is negligible and non zero only near the boundaries of the system, so that by (21) $p_{zz}(\mathbf{r})$ is nearly constant for $z \geq \bar{z}$. After the displacement the wall originally at $z = L_z$ is located at $z = L_z + \lambda(L_z - \bar{z})$. The work done on the system when the volume changes by δV is according to (24):

$$\delta W = -\lambda L_x L_y \int_{\bar{z}}^{L_z} dz p_{zz}(z) \quad (30)$$

We again express $\mathbf{f}(\mathbf{r})$ in terms of distribution functions with the help of (8) and compute the work of deformation using (23)

$$\delta W = \int d\mathbf{r} \lambda(z - \bar{z})\theta(z - \bar{z}) \left\{ \sum_{\beta} \frac{\partial}{\partial r_\beta} [T_s \tilde{\Gamma}_{z\beta}^{-1}(\mathbf{r})\rho(\mathbf{r})] + \int d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}') \frac{\partial w(\mathbf{r} - \mathbf{r}')}{\partial z} \right\} \quad (31)$$

Equating (30) and (31) and differentiating both sides w.r.t. \bar{z} we find:

$$p_{zz}(\bar{z}) L_x L_y = - \int d\mathbf{r} \theta(z - \bar{z}) \left\{ \sum_{\beta} \frac{\partial}{\partial r_\beta} [T_s \tilde{\Gamma}_{z\beta}^{-1}(\mathbf{r})\rho(\mathbf{r})] + \int d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}') \frac{\partial w(\mathbf{r} - \mathbf{r}')}{\partial z} \right\} \quad (32)$$

Integrating by parts the first term and recalling that the surface terms vanish outside the finite volume of the system we get:

$$p_{zz}(\bar{z}) = \int \frac{d\mathbf{r}}{L_x L_y} \left\{ \delta(z - \bar{z}) T_s \tilde{\Gamma}_{zz}^{-1}(\mathbf{r})\rho(\mathbf{r}) - \theta(z - \bar{z}) \int d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}') \frac{\partial w(\mathbf{r} - \mathbf{r}')}{\partial z} \right\} \quad (33)$$

Finally, we let $L_x \rightarrow \infty$ and $L_y \rightarrow \infty$ transform the formula (see Baus-Lovett²⁷) and obtain the final form:

$$p_{zz}(\bar{z}) = T_s \tilde{\Gamma}_{zz}^{-1}(\bar{z}) \rho(\bar{z}) - \int dz \int d\mathbf{r}' \theta(z - \bar{z}) \theta(\bar{z} - z') \rho^{(2)}(\mathbf{r}, \mathbf{r}') \frac{z - z'}{|\mathbf{r} - \mathbf{r}'|} w'(|\mathbf{r} - \mathbf{r}'|) \quad (34)$$

As discussed by Baus and Lovett the meaning of such an equation is that the pressure $p_{zz}(\bar{z})$ can be measured by evaluating the first term at any plane \bar{z} inside the system and the interaction contribution due to the direct forces acting across the \bar{z} plane so that particles at z and at z' are on opposite sides of the mathematical surface at \bar{z} (i.e. for $z > \bar{z}$ and $z' < \bar{z}$). An analogous formula has been derived by Solon et al.

$$p_{zz}(\bar{z}) = \frac{T_s \rho(\bar{z})}{\tilde{\Gamma}_{zz}(\bar{z})} - 2\pi \int_{\bar{z}}^{\infty} dz \int_0^{\bar{z}} dz' \int_0^{\infty} dR R \rho^{(2)}(z, z', R) \frac{z - z'}{\sqrt{(z - z')^2 + R^2}} w'(z, z', R) \quad (35)$$

On the other hand if $\bar{z} \rightarrow \infty$ the density $\rho(\bar{z})$ becomes uniform and the formula above simplifies:

$$p = T_s \frac{\rho_b}{\tilde{\Gamma}_b} - \frac{2}{3} \pi \rho_b^2 \int_0^{\infty} dr r^3 g_b(r) w'(r) \quad (36)$$

with

$$\tilde{\Gamma}_b = 1 + \frac{4}{3} \frac{\tau}{\gamma} \pi \rho_b \int_0^{\infty} dr r^2 g_b(r) [w''(r) + 2 \frac{w'(r)}{r}] \quad (37)$$

where the subscript b denotes the bulk value of the corresponding quantity.

B. Surface tension of a planar interface

We are, now, interested in deriving a formula for the surface tension of a planar interface normal to the z direction and separating two different phases. The surface tension, γ , is computed from the mechanical definition of work done on the system as a consequence of an isothermal change, δA , of the area A of the interface:

$$\delta W = -p_V \delta V + \gamma \delta A \quad (38)$$

In order to compute γ , we remark that by symmetry the pressure tensor is diagonal, depends only on the z coordinate and can be represented by only two functions: the normal component $p_N(z) = p_{zz}(z)$ and the tangential component $p_T(z) = p_{xx}(z) = p_{yy}(z)$, which are not equal as in the bulk because the latter includes the tension of the interface. Given a rectangular cuboid of base area A and height L , we follow a simple argument by Rowlinson and Widom³¹ to compute the work necessary to increase by an amount δA the area without changing the box volume: it is the sum of two contributions, a) the work necessary to keep the volume constant by applying during this process a normal pressure p_N to the stretched interface and b) the tangential work to stretch the interface. Assuming that p_N does not change with z due to the condition of hydrostatic equilibrium, we write:

$$\delta W = -p_N A \delta L - \delta A \int_{-L/2}^{L/2} dz p_T(z)$$

and since the volume variation must be zero, to linear order we have $\delta V = A \delta L + L \delta A = 0$, we conclude that $\delta L = -L \delta A / A$ and

$$\delta W = \delta A \int_{-L/2}^{L/2} dz [p_N - p_T(z)], \quad (39)$$

and identify γ with the integral in (39). Using the strain-stress formalism we can derive the same result and compute explicitly the pressure components by considering the work done by the internal forces:

$$\begin{aligned} \delta W &= - \int_V d^3 \mathbf{r} [p_N(z) \delta \epsilon_{zz} + p_T(z) \delta \epsilon_{xx} + p_T(z) \delta \epsilon_{yy}] \\ &= - \frac{1}{3} \int_V d^3 \mathbf{r} \left((p_N(z) + 2p_T(z)) [\delta \epsilon_{zz} + \delta \epsilon_{xx} + \delta \epsilon_{yy}] - (p_N(z) - p_T(z)) [\delta \epsilon_{xx} + \delta \epsilon_{yy} - 2\delta \epsilon_{zz}] \right). \end{aligned} \quad (40)$$

The first term represents the trace of the pressure tensor and provides average pressure $p_{av}(z) = (p_N(z) + 2p_T(z))/3$ of the non-uniform system. Let us now assume a displacement of the form: $\delta \mathbf{s}(\mathbf{r}) = \lambda(x, 0, -z)$ corresponding to an isochoric process, i.e. $\nabla \cdot \delta \mathbf{s}(\mathbf{r}) = 0$, and to a relative area change $\frac{\delta A}{A} = \lambda$ of the surface normal to the z-direction, so that (40) can be written as:

$$\delta W = \lambda \int_V d^3 \mathbf{r} (p_N(z) - p_T(z)) = \delta A \int dz (p_N(z) - p_T(z)) = \gamma \delta A. \quad (41)$$

We, now, perform the calculations of the work done by the external force ($\delta W = \int_V d\mathbf{r} \mathbf{f} \cdot \delta \mathbf{s}(\mathbf{r})$) and equate it to $\delta W = \gamma \delta A$. We obtain the following expression for the surface tension:

$$\gamma = \frac{1}{A} \int_V d\mathbf{r} [x f_x(\mathbf{r}) - z f_z(\mathbf{r})] \quad (42)$$

and proceed to eliminate the components of \mathbf{f} in favor of the microscopic distribution functions in (42) using (8). The resulting expression of the surface tension can be divided in two pieces as $\gamma = \gamma^{active} + \gamma^{direct}$: the first one contains ideal, swim and indirect contributions and after integrating by parts reads:

$$\gamma^{active} = \frac{T_s}{A} \int_V d\mathbf{r} \sum_{\beta} \frac{\partial}{\partial r_{\beta}} [x \tilde{\Gamma}_{x\beta}^{-1}(\mathbf{r}) \rho(\mathbf{r}) - z \tilde{\Gamma}_{z\beta}^{-1}(\mathbf{r}) \rho(\mathbf{r})] - \frac{T_s}{A} \int_V d\mathbf{r} \sum_{\beta} [\delta_{\beta x} \tilde{\Gamma}_{x\beta}^{-1}(\mathbf{r}) - \delta_{\beta z} \tilde{\Gamma}_{z\beta}^{-1}(\mathbf{r})] \rho(\mathbf{r}). \quad (43)$$

Taking into account that the first integral in the r.h.s. vanishes we obtain:

$$\gamma^{active} = \frac{T_s}{A} \int_V d\mathbf{r} [\tilde{\Gamma}_{zz}^{-1}(\mathbf{r}) - \tilde{\Gamma}_{xx}^{-1}(\mathbf{r})] \rho(\mathbf{r}). \quad (44)$$

The second contribution to the surface tension, stemming from direct interactions and represented by the last term in the r.h.s. of (8), is a standard calculation in equilibrium fluids and results in the following expression:

$$\gamma^{direct} = \frac{1}{2A} \int d\mathbf{r} \int d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}') \left(\frac{(x - x')^2 - (z - z')^2}{|\mathbf{r} - \mathbf{r}'|} \right) \frac{\partial w(\mathbf{r} - \mathbf{r}')}{\partial r} \quad (45)$$

By putting together (44) and (45) we see that this prescription for the surface tension gives the same result up to order τ/γ as formula(20) which was obtained by an isochoric deformation of the system and coordinate rescaling.

In order to evaluate γ^{active} we need the explicit form of the diagonal $\tilde{\Gamma}_{\alpha\beta}$ matrix elements:

$$\tilde{\Gamma}_{N(T)}(z) = 1 + \frac{\tau}{\gamma} \int d\mathbf{r}' w_{zz(xx)}(\mathbf{r}, \mathbf{r}') \rho(z') g(\mathbf{r}, \mathbf{r}'). \quad (46)$$

Using (44) and (45) and the second equality in (41) we may identify the active and passive part of the normal and tangential pressure tensor as:

$$\left(\begin{array}{c} p_N^{active}(z) \\ p_T^{active}(z) \end{array} \right) = T_s \rho(z) \left(\begin{array}{c} \frac{1}{\tilde{\Gamma}_N(z)} \\ \frac{1}{\tilde{\Gamma}_T(z)} \end{array} \right) \quad (47)$$

and

$$\left(\begin{array}{c} p_N^{direct}(z) \\ p_T^{direct}(z) \end{array} \right) = -\frac{1}{2} \rho(z) \int d\mathbf{r}' g(\mathbf{r}, \mathbf{r}') \rho(z') \left(\begin{array}{c} (z - z')^2 \\ (x - x')^2 \end{array} \right) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \frac{\partial w(\mathbf{r} - \mathbf{r}')}{\partial r} \quad (48)$$

Notice that the active pressure is higher in the low-density region than in the dense phase because of the mobility reduction⁷.

Summing the two expressions we obtain the total surface tension $p_{N(T)} = p_{N(T)}^{active}(z) + p_{N(T)}^{direct}(z)$. Notice that the scalar pressure defined as: $p_{av}(z) = \frac{1}{3} Tr p_{\alpha\beta}(z)$ is not constant through the interface, whereas $p_N(z)$ must be constant in order to ensure mechanical equilibrium in the absence of external stabilizing fields.

To conclude, we have seen that the activity modifies the ideal gas term of the pressure by the presence of the friction matrix $\tilde{\Gamma}_{\alpha\beta}(\mathbf{r})$, besides modifying the density distribution and the pair correlation function. This trend has been observed by the three methods considered in all the scrutinized quantities, namely the surface tension and the components of the pressure tensor.

C. Comment about the swim pressure of Solon et al.

In order to make contact with the approach proposed by Solon et al.^{4,13} we compare our result (27) with their expression for the swim pressure which in the present notation reads:

$$p^{swim} = \frac{\rho}{d} \tau \gamma v_0 v(\rho)$$

where $v(\rho)$ and v_0 are the average speeds of a particle along its direction of propulsion with and without interparticle interactions, respectively. In the interacting case, these authors express the density dependent velocity as $v(\rho) = (v_0 + I_2/\rho)$ where I_2 is expressed in terms of the pair potential. Separating the swim pressure and identifying $T_a/\gamma = D_a = v_0^2 \tau/d$ we have

$$p^{swim} = \rho \frac{T_a}{d} \tau \gamma v_0 (v_0 + (v(\rho) - v_0)) = \rho T_a + \frac{\rho}{d} \tau \gamma v_0 (v(\rho) - v_0). \quad (49)$$

Such a result can be compared with our expression for the active pressure (27) in the case where, for the sake of simplicity we set $T_t = 0$ and assume a uniform density so that $p^{active} = T_a \frac{\rho}{d} \sum_{\alpha=1}^d \tilde{\Gamma}_{\alpha\alpha}^{-1}$. By using a result recently derived³², we relate the variance of the velocity of the particles in the UCNA model to the inverse friction matrix $\tilde{\Gamma}$ according to $\sum_{\alpha=1}^d \langle v_\alpha v_\alpha \rangle = \frac{D_a}{\tau} \sum_{\alpha=1}^d \tilde{\Gamma}_{\alpha\alpha}^{-1}$ and rewrite the active pressure as:

$$p^{active} = \rho \frac{T_a}{d} \sum_{\alpha=1}^d [1 + (\tilde{\Gamma}_{\alpha\alpha}^{-1} - 1)] \approx \rho T_a + \frac{\rho}{d} \tau \gamma [\langle v_\alpha v_\alpha \rangle - \langle v_\alpha^0 v_\alpha^0 \rangle]. \quad (50)$$

with $\langle v_\alpha^0 v_\alpha^0 \rangle \equiv D_a/\tau$. One can observe the striking similarity between eqs. (49) and (50), in both appears the difference between the effective velocity v and the velocity of an isolated particle, so that in both equations the excess term vanishes when $\rho \rightarrow 0$.

VI. CONCLUSIONS

We have studied different routes to pressure for a particular model system of active particles. We have focused on an argument which has recently generated some debate: whether the pressure in active fluids is a state function or not. By an analysis of models with anisotropic interactions or with quorum sensing, it has been reported that this is generally not the case^{4,13}. Differently for our model we have found that, within the limits of our approximations, the pressure of an assembly of active particles with repulsive spherical interactions is a state function and can be computed from a partition function and this coincides with other definitions of pressure obtained from a mechanical perspective. Very recently, Speck³³ using a stochastic thermodynamic approach has derived expressions for the pressure and the surface tension of active Brownian particles that agree with ours.

Summarizing we have computed the pressure and the surface tension of an active system within the UCNA and found that the results of different methods are in agreement as long as we limit ourselves to first order in the relaxation time of the active noise. Moreover, all the quantities reduce smoothly to their equilibrium values when this non-equilibrium parameter vanishes. In a forthcoming publication, we shall also show that for a simple model system of harmonic dumbbells these theoretical predictions are exact and the agreement between different methods is valid to any order. Our results also suggest to compare the pressure obtained numerically in other simple models of active particles (e.g. in active Brownian and run and tumble particles) and check if the agreement among different definitions of pressure is preserved when the relaxation time of the noise is small.

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Appendix A: Derivation of the mobility term in the BGY equation

The stationary distribution $P_N(\mathbf{r}_1, \dots, \mathbf{r}_N)$ obeys a first order partial differential equation which relates the probability distribution to the potential \mathcal{U}_{total} and from this equation, one obtains equations for the marginalized distribution functions $P_N^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) = \int d\mathbf{r}_{n+1} \dots d\mathbf{r}_N P_N(\mathbf{r}_1, \dots, \mathbf{r}_N)$ of different orders (see ref.¹⁵). In particular, one obtains:

$$T_s \int \int d\mathbf{r}_2 \dots d\mathbf{r}_N \sum_{\beta} \sum_k \frac{\partial}{\partial r_{\beta k}} [\Gamma_{\alpha 1, \beta k}^{-1}(\mathbf{r}_1, \dots, \mathbf{r}_N) P_N(\mathbf{r}_1, \dots, \mathbf{r}_N)] = -P_N^{(1)}(\mathbf{r}_1) \frac{\partial u(\mathbf{r}_1)}{\partial r_{\alpha 1}} - (N-1) \int d\mathbf{r}_2 P_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \frac{\partial w(\mathbf{r}_1 - \mathbf{r}_2)}{\partial r_{\alpha 1}}. \quad (\text{A1})$$

We write the l.h.s of (A1) as the sum of two contributions $D_{\alpha 1, \beta 1}(\mathbf{r}_1)$ and $\sum_{\beta, k} E_{\alpha 1, \beta k}(\mathbf{r}_1)$, diagonal (D) and off-diagonal (E) terms, respectively :

$$D_{\alpha 1, \beta 1}(\mathbf{r}_1) \equiv \frac{\partial}{\partial r_{\alpha 1}} T_s \int \int d\mathbf{r}_2 \dots d\mathbf{r}_N \Gamma_{\alpha 1, \beta 1}^{-1}(\mathbf{r}_1, \dots, \mathbf{r}_N) P_N(\mathbf{r}_1, \dots, \mathbf{r}_N) \quad (\text{A2})$$

and

$$\sum_{\beta} \sum_{k \neq 1} E_{\alpha 1, \beta k}(\mathbf{r}_1) \equiv T_s \int \int d\mathbf{r}_2 \dots d\mathbf{r}_N \sum_{\beta} \sum_{k \neq 1} \frac{\partial}{\partial r_{\beta k}} [\Gamma_{\alpha 1, \beta k}^{-1}(\mathbf{r}_1, \dots, \mathbf{r}_N) P_N(\mathbf{r}_1, \dots, \mathbf{r}_N)] \quad (\text{A3})$$

In the limit of τ/γ small we may approximate the inverse matrix Γ as

$$\Gamma_{\alpha i, \beta k}^{-1} \approx \left(\delta_{\alpha \beta} - \frac{\tau}{\gamma} u_{\alpha \beta}(\mathbf{r}_i) - \frac{\tau}{\gamma} \sum_j w_{\alpha \beta}(\mathbf{r}_i - \mathbf{r}_j) \right) \delta_{ik} + \frac{\tau}{\gamma} w_{\alpha \beta}(\mathbf{r}_i - \mathbf{r}_k) (1 - \delta_{ik}). \quad (\text{A4})$$

where $u_{\alpha\beta}(\mathbf{r}) \equiv \frac{\partial^2 u(\mathbf{r})}{\partial r_\alpha \partial r_\beta}$ and $w_{\alpha\beta}(\mathbf{r}) \equiv \frac{\partial^2 w(\mathbf{r})}{\partial r_\alpha \partial r_\beta}$. Substituting we obtain the diagonal term

$$D_{\alpha 1, \beta 1}(\mathbf{r}_1) \approx T_s \frac{\partial}{\partial r_{\alpha 1}} \left(P_1(\mathbf{r}_1) [\delta_{\alpha\beta} - \frac{\tau}{\gamma} u_{\alpha\beta}(\mathbf{r}_1)] - \frac{\tau}{\gamma} (N-1) \int d\mathbf{r}' P_2(\mathbf{r}_1, \mathbf{r}') w_{\alpha\beta}(\mathbf{r}_1 - \mathbf{r}') \right) \quad (\text{A5})$$

whereas the individual contributions from the off diagonal elements ($k \neq 1$) are:

$$\sum_{\beta} E_{\alpha 1, \beta k}(\mathbf{r}_1) = T_s \frac{\tau}{\gamma} \int d\mathbf{q}_k \sum_{\beta} \frac{\partial}{\partial q_{\beta k}} \left(P_2(\mathbf{r}_1, \mathbf{q}_k) w_{\alpha\beta}(\mathbf{r}_1 - \mathbf{q}_k) \right) \quad (\text{A6})$$

By integrating with respect to $q_{\beta k}$ we find

$$\sum_{\beta} E_{\alpha 1, \beta k}(\mathbf{r}_1) \approx \frac{\tau}{\gamma} \int dq_{xk} dq_{yk} dq_{zk} \left(P_2(\mathbf{r}_1, \mathbf{q}_k) \sum_{\beta} w_{\alpha\beta}(\mathbf{r}_1 - \mathbf{q}_k) \right) [\delta(q_{\beta k} - L_{\beta}^+) - \delta(q_{\beta k} - L_{\beta}^-)] \quad (\text{A7})$$

where L_{β}^{\pm} are the coordinates of the boundaries of the system in the β direction. We discard such a boundary term, i.e. we set $\sum_{\beta} E_{\alpha 1, \beta k}(\mathbf{r}_1) = 0$, and using (A1) and (A4), (A5), (A7) obtain the result (7) expressed in terms of density distributions.

Appendix B: Approximate form of the inverse matrix Γ^{-1}

Using eq. (A4) we compute the average of the trace of the inverse matrix Γ which can be written as:

$$\sum_i^N \sum_{\alpha}^d \langle \Gamma_{\alpha i, \alpha i}^{-1} \rangle \approx N \sum_{\alpha}^d \int d\mathbf{r} \left(P_1(\mathbf{r}) [1 - \frac{\tau}{\gamma} u_{\alpha\alpha}(\mathbf{r})] - \frac{\tau}{\gamma} (N-1) \int d\mathbf{r}' P_2(\mathbf{r}, \mathbf{r}') w_{\alpha\alpha}(\mathbf{r} - \mathbf{r}') \right) \quad (\text{B1})$$

and switching to density variables $\rho(\mathbf{r}) = N P_N^{(1)}(\mathbf{r})$ and $\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r}) \rho(\mathbf{r}') g(\mathbf{r}, \mathbf{r}') = N(N-1) P_N^{(2)}(\mathbf{r}, \mathbf{r}')$, the one- and two-particle distribution functions, respectively we find:

$$\sum_i^N \sum_{\alpha}^d \langle \Gamma_{\alpha i, \alpha i}^{-1} \rangle \approx \int d\mathbf{r} \rho(\mathbf{r}) \tilde{\Gamma}_{\alpha\alpha}^{-1}(\mathbf{r}) \quad (\text{B2})$$

where $\tilde{\Gamma}$ is the $d \times d$ matrix defined by eq.(9).

Appendix C: Evolution of operators

The time evolution of the system is given by the Fokker-Planck equation which reads (see ref.¹⁵):

$$\frac{\partial P_N(\mathbf{r}_1, \dots, \mathbf{r}_N; t)}{\partial t} = - \sum_{\alpha i} \frac{\partial}{\partial r_{\alpha i}} \sum_{\beta k} \Gamma_{\alpha i, \beta k}^{-1} \left(\frac{1}{\gamma} F_{\beta k} P_N - D \sum_{\gamma j} \frac{\partial}{\partial r_{\gamma j}} [\Gamma_{\gamma j, \beta k}^{-1} P_N] \right) \quad (\text{C1})$$

where Greek indexes stand for Cartesian components. Consequently the evolution equation of the statistical average $\langle \mathcal{O}(t) \rangle \equiv \int d^N \mathbf{r} P_N(\mathbf{r}_1, \dots, \mathbf{r}_N; t) \mathcal{O}(\mathbf{r}_1, \dots, \mathbf{r}_N)$ of an arbitrary operator \mathcal{O} of the variables \mathbf{r}_i is given by

$$\frac{d\langle \mathcal{O} \rangle}{dt} = \int d^N \mathbf{r} P_N(\mathbf{r}_1, \dots, \mathbf{r}_N; t) \sum_{\alpha i} \sum_{\beta k} \Gamma_{\alpha i, \beta k}^{-1} \left(\frac{1}{\gamma} F_{\beta k} \frac{\partial \mathcal{O}}{\partial r_{\alpha i}} + D \frac{\partial}{\partial r_{\alpha i}} \sum_{\gamma j} \Gamma_{\gamma j, \beta k}^{-1} \frac{\partial \mathcal{O}}{\partial r_{\gamma j}} \right) \quad (\text{C2})$$

Appendix D: Derivative of effective free energy with respect to the enclosing volume

Performing the derivative of the configurational integral Z_N requires taking into account that the limits of the integrals defining Z_N depend on the system volume, V . To properly take the derivative we non-dimensionalize each particle coordinate by the size of the box, by making the change $\mathbf{r}_i \rightarrow L \mathbf{q}_i$, where the $-\infty \leq q_{i\alpha} \leq \infty$. We evaluate the derivative $p_t = T_s \frac{\partial \ln Z_N}{\partial V}$. and show that up to first order in the perturbation parameter τ/γ this quantity coincides

with the mechanical pressure and with the virial pressure. We assume that \mathcal{U}_{total} includes only pairwise forces and a confining external potential with the following scaling on the linear size of the system, L :

$$\mathcal{U}_{total} = \mathcal{U}_{int}(\mathbf{r}_1, \dots, \mathbf{r}_N) + U_{wall}\left(\frac{\mathbf{r}_1}{L}, \dots, \frac{\mathbf{r}_N}{L}\right) \quad (\text{D1})$$

U_{wall} is a smooth function becoming infinite when $r_\alpha \rightarrow \pm\infty$, in particular if $|r_\alpha| > L$ so that the density becomes exponentially small. The volume dependence of Z_N is set by the typical volume $V = L^3$ since the domain of integration is infinite but L is the typical size of the container. In order to obtain the formula (18) we rescale the coordinates $\mathbf{r}_i \rightarrow L\mathbf{q}_i$.

$$Z_N = L^{3N} \int_{-\infty}^{\infty} d\mathbf{q}_1 \dots \int_{-\infty}^{\infty} d\mathbf{q}_N \exp\left(-\frac{\mathcal{H}(L\mathbf{q}_1, \dots, L\mathbf{q}_N)}{T_s}\right) \quad (\text{D2})$$

and evaluate the derivative

$$\frac{\partial Z_N}{\partial V} = \frac{N}{V} Z_N - V^N \frac{1}{T_s} \int_{-\infty}^{\infty} d\mathbf{q}_1 \dots \int_{-\infty}^{\infty} d\mathbf{q}_N \exp\left(-\frac{\mathcal{H}(L\mathbf{q}_1, \dots, L\mathbf{q}_N)}{T_s}\right) \frac{\partial \mathcal{H}(L\mathbf{q}_1, \dots, L\mathbf{q}_N)}{\partial L} \quad (\text{D3})$$

As a consequence of the scaling assumed for the wall potential, the derivative of the wall potential drops, because $U_{wall}(\frac{\mathbf{r}_1}{L}, \dots, \frac{\mathbf{r}_N}{L}) = U_{wall}(\mathbf{q}_1, \dots, \mathbf{q}_N)$ does not contain any L dependence and we obtain:

$$\frac{\partial Z_N}{\partial V} = \frac{N}{V} Z_N - \frac{1}{3T_s} V^N \frac{L}{V} \int_{-\infty}^{\infty} d\mathbf{q}_1 \dots \int_{-\infty}^{\infty} d\mathbf{q}_N \exp\left(-\frac{\mathcal{H}(L\mathbf{q}_1, \dots, L\mathbf{q}_N)}{T_s}\right) \sum_i \mathbf{q}_i \cdot \frac{\partial \mathcal{H}_1(L\mathbf{q}_1, \dots, L\mathbf{q}_N)}{\partial (L\mathbf{q}_i)} \quad (\text{D4})$$

where now:

$$\mathcal{H}_1(\mathbf{r}_1, \dots, \mathbf{r}_N) = \mathcal{U}_{int}(\mathbf{r}_1, \dots, \mathbf{r}_N) + \frac{\tau}{2\gamma} \sum_k \left(\frac{\partial \mathcal{U}_{total}(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\partial \mathbf{r}_k} \right)^2 - T_s \ln |\det(I + \frac{\tau}{\gamma} \nabla \nabla \mathcal{U}_{total}(\mathbf{r}_1, \dots, \mathbf{r}_N))| \quad (\text{D5})$$

Notice that the wall potential W is absent in the linear term. We restore, now, the original dimensional variables in the integrals:

$$p_t = T_s \frac{1}{Z_N} \frac{\partial Z_N}{\partial V} = T_s \frac{N}{V} - \frac{1}{3V} \frac{1}{Z_N} \int d\mathbf{r}_1 \dots \int d\mathbf{r}_N \exp\left(-\frac{\mathcal{H}(\mathbf{r}_1, \dots, \mathbf{r}_N)}{T_s}\right) \sum_i \mathbf{r}_i \cdot \frac{\partial \mathcal{H}_1(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\partial \mathbf{r}_i} \quad (\text{D6})$$

In analogy with equilibrium statistical mechanics and by dimensional considerations, we have identified the volume derivative of the logarithm of the partition function with a pressure, p_t , which reads:

$$p_t = \frac{NT_s}{V} - \frac{1}{3V} \left\langle \sum_i \mathbf{r}_i \cdot \frac{\partial \mathcal{U}_{int}}{\partial \mathbf{r}_i} \right\rangle - \frac{1}{3V} \left\langle \sum_i \mathbf{r}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} \left[\frac{\tau}{2\gamma} \sum_k \left(\frac{\partial \mathcal{U}_{total}(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\partial \mathbf{r}_k} \right)^2 - T_s \ln |\det(I + \frac{\tau}{\gamma} \nabla \nabla \mathcal{U}_{total}(\mathbf{r}_1, \dots, \mathbf{r}_N))| \right] \right\rangle. \quad (\text{D7})$$

Proof of the equivalence with the virial pressure: in order to prove that p_t has a physical meaning, we must ascertain whether it agrees with the pressure p_V obtained by the virial MVE method. Apparently, the formulas disagree, but if we consider only the first order expansion in the parameter τ/γ of the previous formula the two methods are in agreement. We start by rewriting

$$p_t = \frac{NT_s}{V} \int_V d\mathbf{r}_1 \dots \int_V d\mathbf{r}_N P_N(\mathbf{r}_1, \dots, \mathbf{r}_N) - \frac{1}{3V} \sum_i \int d\mathbf{r}_1 \dots \int d\mathbf{r}_N P_N(\mathbf{r}_1, \dots, \mathbf{r}_N) \mathbf{r}_i \cdot \frac{\partial \mathcal{H}_1}{\partial \mathbf{r}_i} \quad (\text{D8})$$

and notice that to first order in τ/γ we have

$$\begin{aligned} P_N(\mathbf{r}_1, \dots, \mathbf{r}_N) \sum_{\beta j} \left(\frac{\tau}{\gamma} \frac{\partial \mathcal{U}_{total}(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\partial r_{\beta j}} \frac{\partial^2 \mathcal{U}_{total}}{\partial r_{\alpha i} \partial r_{\beta j}} - T_s \frac{\partial}{\partial r_{\alpha i}} \ln \det \Gamma \right) \approx \\ -T_s \frac{\tau}{\gamma} \sum_{\beta j} \left\{ \left[\frac{\partial}{\partial r_{\beta j}} P_N(\mathbf{r}_1, \dots, \mathbf{r}_N) \right] \frac{\partial^2 \mathcal{U}_{total}}{\partial r_{\alpha i} \partial r_{\beta j}} + P_N(\mathbf{r}_1, \dots, \mathbf{r}_N) \frac{\partial^3 \mathcal{U}_{total}}{\partial r_{\alpha i} \partial r_{\beta j}^2} \right\} \end{aligned} \quad (\text{D9})$$

so that the pressure can be rewritten as

$$p_t \approx \frac{NT_s}{V} \int d\mathbf{r}_1 \dots d\mathbf{r}_N P_N - \frac{1}{3V} \sum_i \int d\mathbf{r}_1 \dots \int_V d\mathbf{r}_N P_N(\mathbf{r}_1, \dots, \mathbf{r}_N) \mathbf{r}_i \cdot \frac{\partial \mathcal{U}_{int}}{\partial \mathbf{r}_i} + \frac{T_s}{3V} \frac{\tau}{\gamma} \int d\mathbf{r}_1 \dots d\mathbf{r}_N \sum_{\alpha i} \sum_{\beta j} \frac{\partial}{\partial r_{\beta j}} [P_N(\mathbf{r}_1, \dots, \mathbf{r}_N) \frac{\partial^2 \mathcal{U}_{total}}{\partial r_{\alpha i} \partial r_{\beta j}}] r_{\alpha i} \quad (D10)$$

and after an integration by parts and discarding a boundary term we obtain

$$p_t = -\frac{1}{3V} \langle \sum_i \mathbf{r}_i \cdot \frac{\partial \mathcal{U}_{int}}{\partial \mathbf{r}_i} \rangle + \frac{T_s}{3V} \int d\mathbf{r}_1 \dots d\mathbf{r}_N \sum_{\alpha i} P_N(\mathbf{r}_1, \dots, \mathbf{r}_N) [\delta_{\alpha\beta} - \frac{\tau}{\gamma} \frac{\partial^2 \mathcal{U}_{total}}{\partial r_{\alpha i}^2}] \quad (D11)$$

After recognising that the first term is the internal virial, and the last term is the first order approximation to the trace of the inverse matrix Γ , we find the result eq. (18) of the main text.

Appendix E: Derivative of effective free energy with respect to the interfacial area

In this case, we shall assume that the system is contained in a box of volume $V = L_x \times L_y \times L_z$, with $L_x = L_y = \sqrt{A}$ and in order to properly take the derivative with respect to the area, while keeping the volume V fixed, we non-dimensionalize each particle coordinate by the transformation:

$$(x_i, y_i, z_i) \rightarrow (\sqrt{A}X_i, \sqrt{A}Y_i, \frac{V}{A}Z_i)$$

and assume $0 \leq (X_i, Y_i, Z_i) \leq 1$ and rewrite the partition function as

$$Z_N = V^N \Pi_i^N \int_0^1 \int_0^1 \int_0^1 dX_i dY_i dZ_i \dots \exp\left(-\frac{\mathcal{H}(\sqrt{A}X_1, \sqrt{A}Y_1, \frac{V}{A}Z_1, \dots)}{T_s}\right) \quad (E1)$$

where \mathcal{H} now contains only the interparticle potentials and not the external potential which is already accounted for by the limits of integration. Now we differentiate the partition function with respect to the area at constant volume and obtain:

$$\frac{\partial Z_N}{\partial A} = -\frac{1}{T_s} V^N \Pi_i^N \int_0^1 \int_0^1 \int_0^1 dX_1 dY_i dZ_i \dots \exp\left(-\frac{\mathcal{H}(\mathbf{r}_1, \dots, \mathbf{r}_N)}{T_s}\right) \sum_i \frac{\partial \mathbf{r}_i}{\partial A} \cdot \frac{\partial \mathcal{H}(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\partial \mathbf{r}_i} \quad (E2)$$

Since the derivatives of the coordinates with respect to A are: $\frac{\partial}{\partial A}(x_i, y_i, z_i) = (\frac{1}{2A}x_i, \frac{1}{2A}y_i, -\frac{z_i}{A})$ we find:

$$\frac{\partial Z_N}{\partial A} = -\frac{1}{T_s} \int_V d\mathbf{r}_1 \dots d\mathbf{r}_N \exp\left(-\frac{\mathcal{H}(\mathbf{r}_1, \dots, \mathbf{r}_N)}{T_s}\right) \sum_i \left[\frac{x_i}{2A} \frac{\partial \mathcal{H}(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\partial x_i} + \frac{y_i}{2A} \frac{\partial \mathcal{H}(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\partial y_i} - \frac{z_i}{A} \frac{\partial \mathcal{H}(\mathbf{r}_1, \dots, \mathbf{r}_N)}{\partial z_i} \right] \quad (E3)$$

Going back to the original coordinates and recalling that the x and y direction are equivalent we obtain the formula:

$$\gamma = -T_s \frac{\partial \ln Z_N}{\partial A} = \frac{1}{A} \langle \sum_i \left[x_i \frac{\partial}{\partial x_i} - z_i \frac{\partial}{\partial z_i} \right] \left(U_{int} + \frac{\tau}{2\gamma} \sum_k \left(\frac{\partial \mathcal{U}_{int}}{\partial \mathbf{r}_k} \right)^2 - T_s \ln |\det(I + \frac{\tau}{\gamma} \nabla \nabla \mathcal{U}_{int})| \right) \rangle \quad (E4)$$

In order to prove the equivalence of the thermodynamic surface tension with its expression given in section V B, we use the same expansion up to linear order in τ/γ as in section D and obtain:

$$\gamma \approx \frac{1}{A} \int_V d\mathbf{r}_1 \dots d\mathbf{r}_N \sum_i \left\{ \left[x_i \frac{\partial U_{int}}{\partial x_i} - z_i \frac{\partial U_{int}}{\partial z_i} \right] P_N - T_s \frac{\tau}{\gamma} \sum_{\beta j} \frac{\partial}{\partial r_{\beta j}} \left[P_N \frac{\partial^2 \mathcal{U}_{int}}{\partial x_i \partial r_{\beta j}} \right] x_i - \frac{\partial}{\partial r_{\beta j}} \left[P_N \frac{\partial^2 \mathcal{U}_{int}}{\partial z_i \partial r_{\beta j}} \right] z_i \right\}. \quad (E5)$$

After an integration by parts we get the result eq. (19) of the main text.